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Spectral oil analyzer

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Abstract. We worked out a spectral oil analyzer, implemented the method of Fourier transform infrared spectroscopy, which allow simultaneous detecting characteristic peaks of water absorption and sulfur-containing substances in oil within the wavelength range from 0.2 to 25.0 μm . The usage of fiber-optic delivering channels makes it possible to produce online industrial probes for the control of chemical composition and concentration, what is demanded at oil producing platforms and oil refinery plants. As identifiers, we used the most intense absorption peaks of water ($\lambda - 1.45 \mu\text{m}$, $1.95 \mu\text{m}$, $3.00 \mu\text{m}$, $6.00 \mu\text{m}$), oil ($\lambda - 1.72 \mu\text{m}$, $2.31 \mu\text{m}$, $3.41 \mu\text{m}$) and sulfur-containing heterocycles ($\lambda - 8.00 \mu\text{m}$). The spectral analyzer consists of a broadband-light source, a flow-cell, a fiber-optic assembly, narrow-band optical filters and photodetectors. For delivering a broadband optical signal, a fiber-optic assembly was developed. It comprises silica fibers and polycrystalline fibers derived from solid solutions of silver and thallium (I) halides. It was calculated the effective area and diameter of each fiber type in the assembly, taking into account attenuation coefficients and overall optical losses of the system. Using eight channels for the probe at the same time, we were able to measure the content of water and sulfur-containing substances in oil in concentrations from 0.1 to 100.0 wt %.

1. Introduction

At present, the water-cut (water content, moisture) of oil products at wells reaches 75% on average, if considering wells in different countries. Both in Russia and abroad, the laboratory method remains the main method for determining the water content in oil at oil producing wells. It has not been changed for many years despite the fact that the error of the determination is unacceptably large. When the water content is high, the relative error is close to 90-100%. Moreover, considerable time is required for determining the water cut.

Among the online methods of oil moisture monitoring, there are two types which are separated according to the principle of measured physical characteristics: optical and electrical methods. The disadvantage of the electrical methods is low sensitivity in the case of considerable gas phase in the samples under study. Optical methods are based on the registration of absorption peaks which are inherent in test media, regardless of their state, and thus providing higher accuracy and rate of analysis.

One of commonly used methods for online moisture monitoring is a method based on measuring the electrical properties of oil-water mixtures using a capacitor probe. At high water-cut levels, such a capacitor probe doesn't give reliable results. Moreover, a change in the oil density leads to a change in



the dielectric constant, what causes the increase of the measurement error. Paraffine depositions on the condenser plates, high influence of the gas factor are the main disadvantages of capacitor probes, what also limits their use [1]. Another principle of water-in-oil content measurement is based on the absorption of microwave radiation by the medium. The microwave radiation (at frequencies above 1 GHz) is intensively absorbed by polar water molecules and, to a much lesser extent, non-polar hydrocarbon molecules. The method allows to determine water in oil with high accuracy covering the entire range (0-100%), although at high water cut values, the accuracy slightly decreases.

The advantage of the method is low impact of the oil composition on the measurement accuracy. The disadvantages are the influence of the salt content in stratum water on the measurement, as well as its high cost [2]. Coriolis flowmeters can be used to determine the water composition. They simultaneously determine the mass flow rate, density, and calculates the percentage of water in oil based on the density of oil and stratum water. The main disadvantage of this method is a significant decrease in the measurement accuracy in the case of heavy oil, when the density of oil is just a little bit different from the density of water. The presence of free gas in the fluid flow also significantly impairs the measurement accuracy. It is important to note, that when we deal with the group of wells, the water and oil densities vary not only from well to well, but they also vary over time.

The second kind of impurities of oil are sulfur-containing substances. Its content can reach 14 vol.%. Sulfur in oil and oil products is presented partly by elemental sulfur, but mainly by various substances – hydrogen sulfide, mercaptans, sulfides, disulfides, thiophenes, and thiophans [3]. Methods for determining sulfur in oil can be divided into 3 groups: methods based on sulfur oxidation and subsequent determination of oxides [4]; methods based on sulfur reduction to H_2S : [5]; spectral methods (x-ray [6], atomic emission [7], optical [3]). All methods of the sulfur determination combine the general principle – sampling oil and its further processing. This approach, firstly, takes a lot of time, and secondly, it is associated with the statistical errors during the extrapolation of the experimental results on the entire volume of test medium.

Infrared spectroscopy is one of the main ways for analyzing oil and oil products. Its advantage is non-destructive technique, what allows using test samples after the analysis. The change in salinity and the presence of gas phases also do not have a significant effect on the measurement accuracy due to the fact that the method is based on detecting the intensity of characteristic absorption peaks of chemical bonds at certain wavelengths that do not change their positions. The use of fiber-optic delivering channels allows expanding the field of method application and implementing industrial online probes for monitoring chemical compositions and concentrations that are in demand at oil-producing and oil-refining stations.

2. Spectral oil analyzer

To quantify the moisture and sulfuric substances content in oil, the authors developed an immersion probe. It is intended for ATR Fourier transform infrared spectroscopy within the range from 1.2 to 6.5 μm . The specified range is justified by the absorption peaks of water at the wavelengths of 1.45 μm , 1.95 μm , 2.94 μm , and 6.02 μm , which are associated with stretching vibrations of OH groups and H–O–H deformation vibrations [8-10]. The main characteristic absorption bands of oil are 2920 cm^{-1} and 2860 cm^{-1} (the wavelengths of 3.42 μm and 3.49 μm , respectively), which are determined by the stretching vibrations of CH groups (namely, CH_2 and CH_3). In the near IR, there are also corresponding absorption bands at 1.725 μm and 2.31 μm [11]. Oil's sulfur-containing substances are represented by thiophenes and thiophans, which have the absorption peak around 8.0 μm , what corresponds to the sulfur vibrations in the molecular ring [3] (figure 1).

Water absorbs most intensively at a wavelength of 2.94 μm , which is 15 times higher than the absorption of radiation at $\lambda = 1.95 \mu m$, while the intensity of the absorption at a wavelength of 6.02 μm is almost not affected by temperature [8]. Thus, the use of the middle infrared range causes the significant increase of the sensitivity of the developed probe. The probe consists of a broadband IR source, a fiber probe, and optical signal detectors [12, 13]. Such fiber probes operate basing on the principles of attenuation total reflectance (ATR). As a sensitive element, we used a “cone” type element made of zinc selenide (the transmission range of 0.2–18 μm) (figure 2).

Fiber assemblies of the probe were made of optical fibers based on dielectric materials – SiO₂ fibers (the transmission range of 1.2–2.5 μm) and silver halide fibers (the transmission range of 2.5–20.0 μm) [14–16].

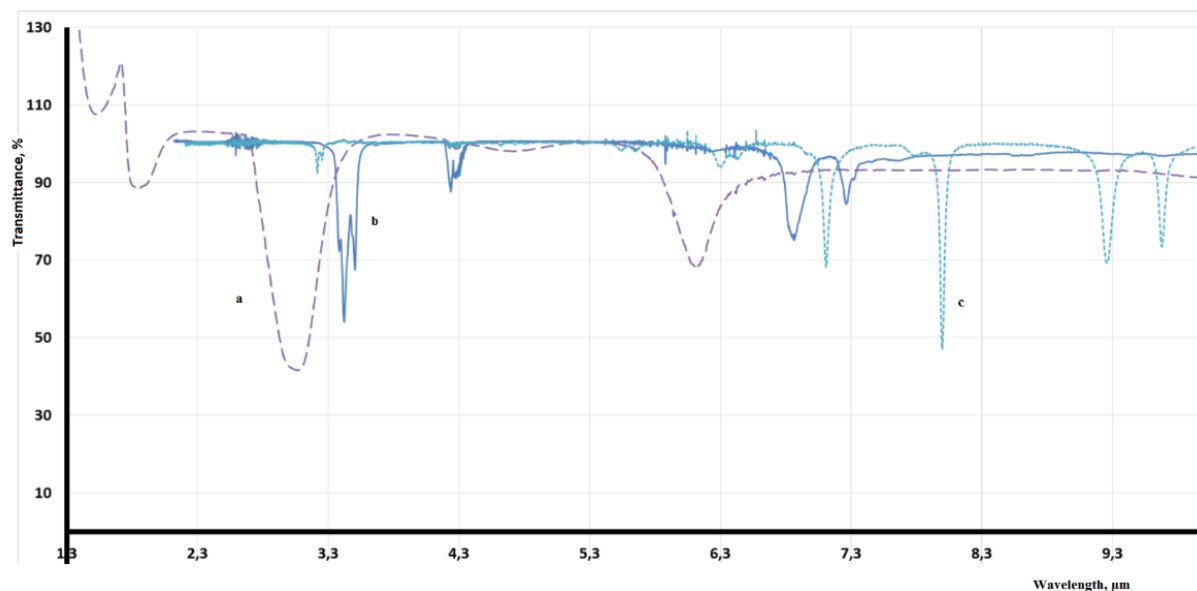


Figure 1. Infrared spectra of water (a), oil (b) and thiophene (c).

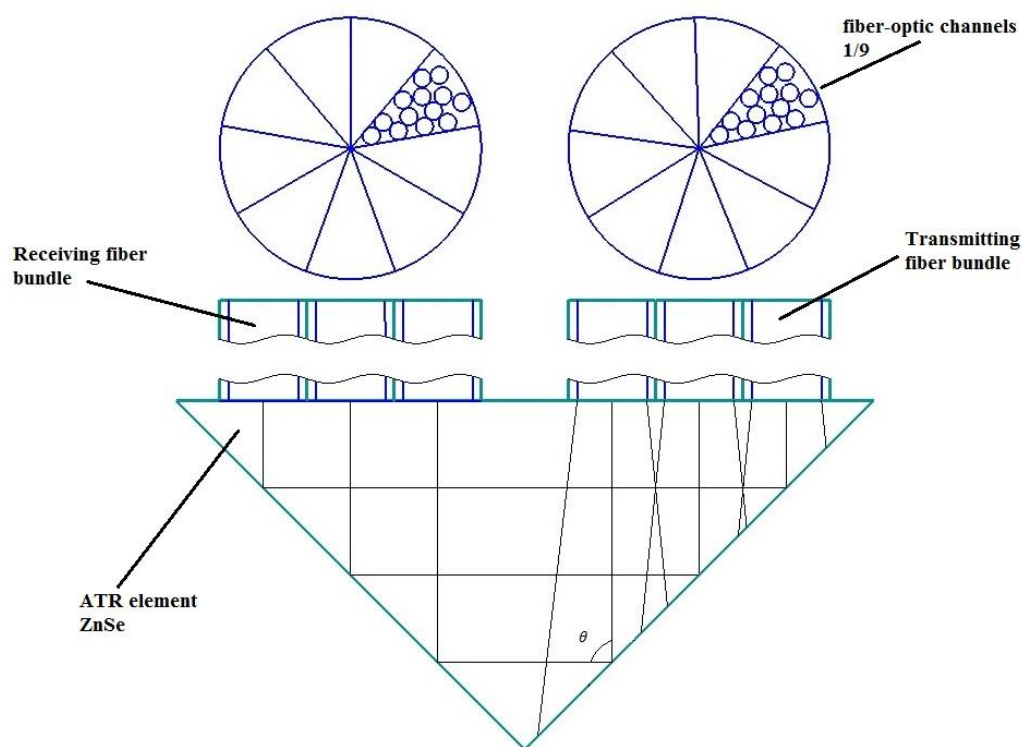


Figure 2. Model of radiation propagation from the transmitting assembly to the receiving assembly through the cone-type ATR-element.

The proposed fiber probe allows setting the units of IR-source and optical signal detector outside the strong field of EM-interference. One more advantage of the probe is that the immersible element does not react with test media. The total optical loss is one of the main functional parameters of sensor systems. It determines the requirements for electro-optical components of the sensor. In this paper, we estimated the total optical loss of a fiber probe depending on the refractive indices, the geometric configuration, and the detected wavelengths. The optical losses of the fiber probe depend on the power distribution efficiency over the receiving end, the optical losses in the fiber channels, and the efficiency of the ATR-element.

Each fiber assembly of the probe comprises nine hexagonally arranged fiber channels: four channels operate in the NIR range for the detection of water absorption peaks, three channels operate in the MIR range for the detection of oil absorption peaks, one channel also operates in the MIR range for detecting absorption peaks of sulfur-containing groups, and one channel operates at a wavelength of 5 μm for the reference signal. The optical fibers are arranged in the form of segments, thus achieving a uniform distribution of power (P_0) from a broadband-light source at the receiving end of the assembly. The ATR-element is a cone with 45° angle between the generator and the base. This form provides the multiple total reflection of optical signals from the cone surface and their transmission from each channel of the transmitting assembly to the corresponding channel of the receiving bundle (figure 2). The radius of the ATR cone base depends on the size of receiving and transmitting bundles and the value of the numerical aperture, and it is determined by the following relationship:

$$R_k \geq \frac{D_b}{1-2 \sin(NA)}, \quad (1)$$

where R_k – the radius of the cone base, D_b – the diameter of the fiber probe, NA is the numerical aperture of the fibers. The parameter NA is calculated by the formula:

$$NA = \sqrt{n_{core}^2 - n_{clad}^2}, \quad (2)$$

where n_{core} – the refractive index of the fiber core, n_{clad} – the refractive index of the fiber cladding. In this case, the numerical aperture should not exceed 0.1.

The calculation of optical losses depending on the refractive index dispersion is presented in table 1. The refractive indices and intrinsic optical losses of AgBr-TII fibers were determined experimentally by authors in [16]. The intrinsic losses of silica fibers were taken from [17]. The authors assumed that the intrinsic optical losses of ZnSe can be neglected because of the short optical path. Fresnel losses were defined as the coefficient of radiation reflection (r) from the media interface. They are calculated using the formula [18]:

$$r = \left(\frac{n_e - n_{core}}{n_e + n_{core}} \right)^2, \quad (3)$$

where n_e – the refractive index of the environment.

Total losses were defined as the sum of Fresnel losses (r) at (N) media interfaces and intrinsic losses (a) due to the attenuation of radiation inside each component of the probe:

$$\Delta P = Nr + a. \quad (4)$$

The power of transmitted radiation in a separate element of the optical scheme was defined as:

$$P_{tr} = P_i \cdot \Delta P. \quad (5)$$

Table 1. Calculated optical losses of the fiber probe.

No. of channel	λ , μm	Material	P_b , %	n_{core}	a , dB/m	r , dB/m	ΔP , dB/m	P_{tr} , %
Transmitting assembly								
1	1.45	Silica	100	1.443	$14 \cdot 10^{-6}$	0.0329	0.0658	93.4
2	1.725	Silica	100	1.442	$14 \cdot 10^{-6}$	0.0328	0.0655	93.4
3	1.95	Silica	100	1.439	$14 \cdot 10^{-6}$	0.0324	0.0648	93.5
4	2.31	Silica	100	1.433	$14 \cdot 10^{-6}$	0.0317	0.0633	93.7
5	2.94	AgBr-TiI	100	2.259	0.2	0.1492	0.4985	50.2
6	3.42	AgBr-TiI	100	2.258	0.2	0.1491	0.4982	50.2
7	5.0	AgBr-TiI	100	2.255	0.2	0.1487	0.4973	50.3
8	6.02	AgBr-TiI	100	2.254	0.2	0.1485	0.4970	50.3
9	8.0	AgBr-TiI	100	2.253	0.2	0.1484	0.4967	50.3
"Cone" type prism								
Prism	1.45	ZnSe	93.4	2.46	-	0.1781	0.3561	60.2
	1.725	ZnSe	93.4	2.45	-	0.1766	0.3533	60.4
	1.95	ZnSe	93.5	2.446	-	0.1761	0.3522	60.6
	2.31	ZnSe	93.7	2.437	-	0.1761	0.3522	60.7
	2.94	ZnSe	50.2	2.436	-	0.1748	0.3496	32.6
	3.42	ZnSe	50.2	2.435	-	0.1747	0.3493	32.7
	5.0	ZnSe	50.3	2.429	-	0.1745	0.3490	32.7
	6.02	ZnSe	50.3	2.425	-	0.1737	0.3473	32.8
	8.0	ZnSe	50.3	2.416	-	0.1731	0.3462	32.9
Receiving assembly								
1	1.45	Silica	60.2	1.443	$14 \cdot 10^{-6}$	0.0329	0.0658	56.2
2	1.725	Silica	60.4	1.442	$14 \cdot 10^{-6}$	0.0328	0.0655	56.5
3	1.95	Silica	60.6	1.439	$14 \cdot 10^{-6}$	0.0324	0.0648	56.7
4	2.31	Silica	60.7	1.433	$14 \cdot 10^{-6}$	0.0317	0.0633	56.8
5	2.94	AgBr-TiI	32.6	2.259	0.2	0.1492	0.4985	16.4
6	3.42	AgBr-TiI	32.7	2.258	0.2	0.1491	0.4982	16.4
7	5.0	AgBr-TiI	32.7	2.255	0.2	0.1487	0.4973	16.4
8	6.02	AgBr-TiI	32.8	2.254	0.2	0.1485	0.4970	16.5
9	8.0	AgBr-TiI	32.9	2.253	0.2	0.1484	0.4967	16.6

The Bouguer-Lambert-Beer law is used for the determination of the moisture content by means of IR-spectroscopy [19]:

$$I = I_0 e^{-\alpha x d}, \quad (6)$$

where I – the intensity of transmitted radiation, I_0 – the intensity of incident radiation, α – the attenuation coefficient, x – the concentration of the substance, d – the optical path. According to this law, the optical density of radiation in the test medium is directly proportional to the concentration of the substance under investigation in this medium, while the attenuation coefficient and the optical path are known.

For ATR-elements, the optical path is calculated as a depth of the radiation penetration into the medium under study d_p [12]:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - n_{21}^2}}, \quad (7)$$

where n_1 – the refractive index of an ATR-element, θ – the radiation incidence angle, n_{21} – the ratio of the ATR-element refractive index to the refractive index of the medium under study. The depth of the radiation penetration varies from 0.25 to 1.9 μm for the considered wavelengths.

The attenuation coefficient of water and sulfur-containing substances in oil was determined experimentally using the following facilities: IR Pestic 21 FTIR spectrometer (Shimadzu) within the wavelength range of 7800-1000 cm^{-1} (1.28-10.0 μm), MCT detector, KBr beam splitter with the resolution of 4 cm^{-1} , ATR-element. The spectrometer was placed in a sealed box for obtaining stable results, with the possibility of sweeping the box with dry N_2 (the volume fraction of water vapor in the nitrogen didn't exceed 0.0007%). The temperature in the laboratory room was maintained within the range of 22-25 $^{\circ}\text{C}$ by means of an air conditioner. We obtained calibration curves, which were used for plotting linear dependences of the optical density on the concentration of water and sulfur in oil at different wavelengths to determine attenuation coefficients (figure 3). The values of the coefficients for each wavelength are shown in table 2.

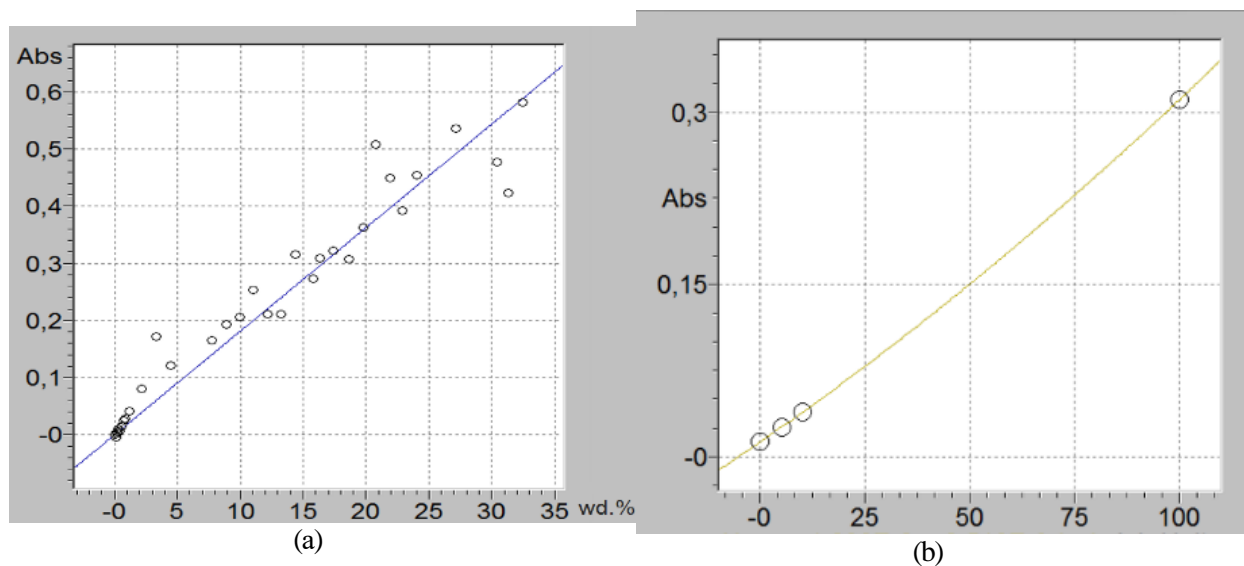


Figure 3. The dependence of optical absorption at a wavelength of 2.94 μm and 8.0 μm on the composition of the water-oil system (a) and thiophene-oil system (b).

Table 2. Experimental values of extinction coefficients.

Wavelength $\lambda, \mu\text{m}$	Absorbing substance	Attenuation coefficient $\alpha, *10^{-3}$
1.45	water	26.44
1.73	oil	21.87
1.95	water	71.37
2.94	water	535.13
3.42	oil	394.72
6.02	water	90.87
8.0	thiophene	197.36

The values of the attenuation coefficient and the depth of penetration, as well as the total optical loss at the corresponding wavelengths will be used to work out a mathematical model for processing optical signals of water and sulfur-containing substances in oil.

Thus, we developed a fiber-optic probe intended to the simultaneous determination of water and sulfur content in the oil. We modeled the optical scheme comprised of transmitting and receiving fiber assemblies, and an ATR-element. The total optical losses of the fiber probe were determined basing on the refractive indices of its components and the test medium. Using an ATR-element, we also calculated the depth of radiation penetration into the oil. Experimentally obtained values of attenuation coefficient will form the basis of a mathematical model for signal processing. All parameters were calculated for a fiber-optic probe with the length of 1 m, which allows deploying the analyzer on the main oil pipeline. If it is necessary to remove the most part of probe electronics, it is required to take into account the rise of intrinsic optical losses in the fiber-optic probe.

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